Macromolecule self-diffusion in poly(ethylene glycol) melts

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Macromolecule self-diffusion in poly(ethylene glycol)s with $M_n = 3 \times 10^2$ to 4×10^4 and $M_w/M_n \approx 1.1$ was investigated by pulsed field gradient nuclear magnetic resonance. Samples with $M_n < 3 \times 10^3$ were characterized by a single self-diffusion coefficient, D. In the fraction with high M_n, a spectrum of values of D was found, its width depending on the diffusion time. The existence of the spectrum of D is explained by the existence of macromolecule dynamic clusters with a finite lifetime in melts. The dependence of the average self-diffusion coefficients on molecular weights is described by a curve with two linear regions, the change in slope occurring where the entanglement network first appears.

(Keywords: self-diffusion; melts; entanglements; macromolecular cluster)

INTRODUCTION

It follows from existing theories[1,2] that, for the dependence of macromolecule self-diffusion coefficients, D, on molecular mass, the following relations should hold: $D \sim M^{-1}$ (ref. 1) when $M < M_c$; $D \sim M^{-2}$ (ref. 2) or $D \sim M^{-2.5}$ (ref. 1) when $M > M_c$; where M_c is a critical molecular mass which is characterized by the appearance of the entanglement net. The results of recent experimental investigations[3,4] of self-diffusion in polyethylene (PE) and polystyrene (PS) melts indicate, however, the absence of any special features near M_c, which differs from the nature of the molecular mass dependence on viscosity[5].

The purpose of the present work was to study macromolecule self-diffusion in poly(ethylene glycol) (PEG) melts with different molecular masses by pulsed field gradient nuclear magnetic resonance (n.m.r.).

EXPERIMENTAL

The experiments were carried out with fractions of poly(ethylene glycol). The weight averages of the molecular weights were from 3×10^2 to 4×10^4. The polydispersity of the samples was $M_w/M_n \leqslant 1.1$. The samples were purchased from Fluka-Buchs, West Berlin.

The self-diffusion coefficients were measured by pulsed field gradient n.m.r. with a home-built spectrometer operating at 60 MHz on hydrogen nuclei. The method of stimulated echo[6] was used. Diffusion spin–echo decays were measured as a function of the pulsed magnetic gradient, g. The largest value of g was equal to 50 T m^{-1}. The technique of obtaining subh pulse gradients has been described in detail previously[7,8]. The constant magnetic field gradient did not exceed 10^{-3} T m^{-1}. The diffusion time, $t_d = \Delta - \delta/3$, where δ is the duration of gradient pulses and Δ is the time interval between them. The δ values were of the order 10^{-5} to 10^{-3} s while t_d varied in the range of 10^{-2} to 2 s.

The high values of g allow one to use both short δ and short intervals between the first two r.f. pulses in the stimulated echo sequence. It gave us the opportunity to exclude the effect of spin–spin relaxation non-exponentiality. The cylindrical samples were evacuated with a high-vacuum pump at 373 K for 2 h. Then they were sealed in 7 mm glass thin-walled tubes. The g direction was perpendicular to sample axis.

We did not observe the disturbing effect of the pulse gradient on the data since the highest value of the magnetic field existing in the sample due to the pulse gradient is equal to $g/2 \approx 0.15$ T, which is much less than the main field $H_0 = 1.5$ T.

All the measurements were conducted at 373 K with the use of digital storage.

RESULTS AND DISCUSSION

Figure 1 shows experimental spin–echo diffusion attenuation $A(g^2)$. The curves are exponential for PEG when $M_n < 3 \times 10^3$, i.e. they can be described by the following relation:

$$A(g^2) = A_0 \exp(-Y^2 g^2 \delta^2 t_d D) \quad (1)$$

where Y is the gyromagnetic ratio. For the samples with $M_n \geqslant 3 \times 10^3$, the diffusion decay shapes are non-exponential and can be described by the following expression:

$$A(g^2) = A_0 \sum_i^n P_i \exp(-Y^2 g^2 \delta^2 t_d D_i) \quad (2)$$

where P_i is that part of the protons with self-diffusion coefficients D_i and $n > 2$. Thus, to describe $A(g^2)$ it is necessary to introduce a set of coefficients D_i. Besides, for samples with $M_n \geqslant 3 \times 10^3$, the shape of diffusion decays appeared to depend on diffusion time t_d (*Figure 2*), the shape of $A(g^2)$ approaching an exponential function with increase of t_d.

A change of the diffusion time t_d in the stimulated echo pulse sequence simultaneously causes a change in the

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